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RECOMMENDED VALUES FOR THE DISTRIBUTION COEFFICIENT (KD) TO BE USED IN DOSE ASSESSMENTS FOR DECOMMISSIONING THE ZION NUCLEAR POWER PLANT

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Table of Contents

List of Tables

Introduction

ZionSolutions is in the process of decommissioning the Zion Nuclear Power Plant. The site contains two reactor Containment Buildings, a Fuel Building, an Auxiliary Building, and a Turbine Building that may be contaminated. The current decommissioning plan involves removing all above grade structures to a depth of 3 feet below grade. The remaining underground structures will be backfilled. The remaining underground structures will contain low amounts of residual licensed radioactive material. An important component of the decommissioning process is the demonstration that any remaining activity will not cause a hypothetical individual to receive a dose in excess of 25 mrem/y as specified in 10CFR20 Subpart E.

The compliance assessment requires prediction of the release and transport of contaminants to the hypothetical individual. Characterization studies by ZionSolutions have identified the following nuclides as being of potential concern (Table 1).

Table 1. Potential Radionuclides of Concern at the Zion Power Plant

Radionuclides	**Radionuclides**	**Radionuclides**	**Radionuclides**	**Radionuclides**	**Radionuclides**
H-3	Co-60	Tc-99	Cs-137	***Eu-155***	Pu-241
C-14	Ni-63	*Ag-108m*	Pm-147	Np-237	Am-241
Fe-55	Sr-90	Sb-125	Eu-152	Pu-238	Am-243
Ni-59	Nb-94	Cs-134	Eu-154	Pu-239/240	Cm-243/244

A key parameter in this assessment is the distribution coefficient (K_d) which is a measure of the amount of the radionuclide that will sorb to the solid media (soil or backfill) in the subsurface environment. The exposure pathway of concern is the groundwater. Groundwater concentration has an inverse relationship with K_d. Thus a lower value of K_d will provide higher groundwater concentrations and a more conservative prediction of dose. BNL (Yim, 2012, Milian, 2014) has conducted site-specific measurements on using local groundwater and samples of site soils and potential backfill materials to assess the K_d value for the contaminants with the expected highest residual concentration (Fe-55, Co-60, Ni-63, Sr-90, and Cs-137) for ZionSolutions. However, there are several other radioactive contaminants (Table 1) that may be present at lower levels that will still require assessment to demonstrate that dose limits are not exceeded. This document reviews the existing literature to recommend a value for K_d when site-specific numbers are not available.

Literature values for K_d show that sorption strongly depends on the contacting media and the geochemical conditions. The backfill selected for disposal will therefore play a huge role in determining the choice of the K_d value. A final decision has not been made on the backfill material at the Zion Power Plant. Materials under consideration include:

- Crushed concrete demolition debris
- Crushed cinder block
- Flowable grout
- Local sand

The concrete and cinder block would be obtained from the building materials removed to three feet below grade and would be free from residual radioactive contamination. Combinations of the above materials are also under consideration.

The first three materials are alkaline and will cause the pH to rise substantially above the local ambient conditions. Based on testing at BNL with materials supplied by ZionSolutions, the pH will initially increase to 10 or 11 for the cementitious materials and grout. Eventually, as the alkali is consumed by buffering reactions the pH will decrease. This is expected to take a minimum of several hundred years depending on the flow rate and buffering capacity of the surrounding soils. Several studies have found that pH is a key geochemical factor in controlling sorption. For this reason consideration must be given to the likely high pH conditions when selecting the Kd value to be used in modeling if a mixture of backfills is used.

Approach

The objective of selecting a K_d value is to choose a value that is reasonably conservative with respect to projected groundwater dose (radionuclide concentrations). This requires a value that is likely to provide a lower bound for K_d. The value for K_d strongly depends on the solid media that contacts the groundwater thus site-specific values are the most representative of actual conditions.

For radionuclides with site-specific data the media with the lowest measured K_d was selected to provide this lower bound. For radionuclides without site-specific data the literature was reviewed to determine the range of K_d values typically found in soils and found in cementitious (high pH) environments. These Kds will be used for initial DUST-MS runs to determine groundwater concentrations at potential well locations. Depending upon the outcome they may be further refined with more site specific or literature data.

Baes and Sharp (Baes and Sharp 1983) were among the first to show that the Kd value for Cs and Sr is log-normally distributed in soils. They applied a log-normal distribution to all elements and this approach is widely used (Sheppard and Thibault, 1990; NRC, 1990). Sheppard and Thibault extended the concept of log-normal distribution to apply to a soil type (sand, loam, clay or organic). This concept is used in this report to determine the 25th percentile value for K_d in soils. The use of the 25th percentile value has been performed in other decommissioning studies at Fermi (Dionne, 2009) and Humboldt Bay (Besson, 2013).

Data

Three types of data are used for the selection of an appropriate Kd for the backfill region at the Zion Nuclear Power Plant. These include site-specific values using local groundwater and soil or concrete samples from the site; literature values for soil environments; and literature values for concrete environments.

Site-specific K_d data:

K_d measurements were performed for ZionSolutions using site-specific groundwater and soil samples (clay, silt, native sand, and disturbed sand – native sand that was excavated during construction of the plant and backfilled around the plant) for six nuclides. Additionally potential backfill materials including two concrete samples (one from the Containment Building and one from the Crib House), two Cinder Block samples from the site, and one low density grout were tested using site-specific groundwater. The elements measured included Fe, Co, Ni, Sr and Cs. Table 2 presents the results of these measurements. Note isotopes of Cs and Ni found in Table 1 are also presented in Table 2 as isotopes will have the same chemical sorption properties.

Table 2 Site-specific K_d values (ml/g) for the Zion Nuclear Power Station

Radionuclide	Site Specific Silt Kd[1] ml/g	Site Specific Silt Clay[1] Kd ml/g	Site Specific Disturbed Sand Kd[1] ml/g	Site Specific Native Sand Kd[1] ml/g	Site Specific Containment Concrete[1] Kd ml/g	Site Specific Crib House Concrete[1] Kd ml/g	Site Specific Cinder Block Kd[2] ml/g	Site Specific Low Density Grout Kd[2] ml/g
Fe-55	8061	17288	2857	5579	16546	17288		
Ni-59	75	136	331	62	3438	8361	177	4,569
Co-60	1161	1161	1161	1161	1161	1161	223	1941
Ni-63	75	136	331	62	3438	8361	177	4,569
Sr-90	2.3	5.7	3.4	2.3	10.4	18.5	23.5	11.8
Cs-134	527	3011	635	615	85	45	249	303
Cs-137	527	3011	635	615	85	45	249	303

[1] Yim, 2012
[2] Milian, 2014

Literature values for Kd in soil environments

Numerous measurements of K_d have been reported in the literature. Key compilations of this data include those by Baes and Sharp (Baes, 1983); Sheppard and Thibault (Sheppard, 1990), Yu (Yu, 1993), the U.S. Nuclear Regulatory Commission (NRC, 2000); and the International Atomic Energy Agency (IAEA, 2010). All of these documents provide statistical parameters to estimate the distribution. Literature values for K_d in soil media from selected sources are presented in Table 3. The first two columns are mean values for K_d presented in (Yu, 1993 and IAEA 2012). For conservatism the 25th percentile in the distribution from the reports (Sheppard, 1990 and NRC, 2000) are also reported in the Table 3. For the Sheppard data the log-normal distribution of the data for sand was used except for Nb-94 and Sb-125 which are the geometrics means because standard deviations were not provided in the Sheppard data. Other soil types were not included because sand, in most cases, has the lowest K_d and the surrounding soil at Zion is primarily sand.

Table 3 Literature soil K_d values for radionuclides of concern at Zion.

Radionuclide	(Yu, 1993) Sand Kd ml/g	(IAEA 2010) Tables 12, 14 Sand or All Soils ml/g	(NRC, 2000) 25th Percentile ml/g	(Sheppard, 1990) Sand 25th Percentile ml/g
H-3		1	0.0431	0.051
C-14	5		1.24	1.76
Fe-55	220	320	34.3	39
Ni-59	400	140	160	148
Co-60	60	640	42.9	9.2
Ni-63	400	140	160	148
Sr-90	15	22	7.49	4.6
Nb-94	160	170	44.6	**164**
Tc-99	0.1	0.23	0.0618	0.04
Ag-108m	90		52.6	27
Sb-125	45	17	43.4	**45**
Cs-134	280	530	92.5	51
Cs-137	280	530	93.4	51
Pm-147		450	94.8	
Eu-152			96.2	
Eu-154			95.2	
Eu-155			95.8	
Np-237	5	35	3.75	1.30
Pu-238	550	400	268	174
Pu-239/240	550	400	267.5	174
Pu-241	550	400	268	174
Am-241	1900	1000	177	333
Am-243	1900	1000	178	333
Cm-243/244	4000	9300	1990	891

The predictions at the 25th percent level of the distribution for the NRC and Sheppard reports are similar. This is because the NRC data set for the distribution is based on, but not limited to the Sheppard data set.

Concrete Environment Kd values

The chemistry of the water will change from an initial value of greater than 11 down to the ambient pH in a crushed concrete environment. The convention of Bradbury and Sarott (1995) describing the three types of chemical environments that all cements progress through is used to understand the data. The following description of the environments has been abbreviated from the initial work by Krupka (Krupka, 1998)

- *Environment I* This environment occurs immediately after the cement hardens and is wetted by infiltrating water The cement pore water is characterized as having a high pH of >12.5, high ionic strength, and high concentrations of potassium and sodium resulting from the dissolution of alkali impurities in the clinker phases. Hydration is still continuing during Environment I with the formation of C-S-H (Calcium- Silicate – Hydrate) and portlandite [$Ca(OH)_2$] The composition of the cement pore fluid is at equilibrium with portlandite during this time. Based on the modeling estimates this environment may last for the first 100 to 10,000 years.

  Environment II During this period, the soluble salts of the alkali metals are all dissolved The pH of the cement pore water is controlled at a value of about 12.5 by the solubility of portlandite. The C-S-H and portlandite are the major solid phases present Environment II may last for a long time Its' duration depends on how much water percolates through the system to dissolve all the slightly soluble portlandite This environment may last from 100-10,000 years to 1,000-100,000 years.

  Environment III The concentration of portlandite has been reduced to such an extent by this period that the solubility of C-S-H now controls the pH of the cement pore fluid The C-S-H starts to dissolve incongruently with a continual decrease in pH At the end of this evolution, Environment III can be conceptualized as leaving only silica (SiO_2) as the solubility control for the pore fluid pH. For the sake of simplicity, the final end point of Environment III can be considered somewhat analogous to the geochemical conditions of the "normal" ambient soil environment.

The important point of this discussion is that the cement will control the pH for hundreds to thousands of years. Thus, if cementitious materials are used for backfill material, a high pH environment will prevail and K_d values are likely to be similar to those found in cement based materials.

Table 4 Preferred distribution coefficients (K_d ml/g) for cement concrete environments (Table 5.1 Krupka, 1998).

	Environment I		Environment II		Environment III	
	Oxidizing Conditions	Reducing Conditions	Oxidizing Conditions	Reducing Conditions	Oxidizing Conditions	Reducing Conditions
Radionuclide	**K_d (ml/g)**					
Am	5000	5000	5000	5000	500	500
C	500	500	100	100	10	10
Cl	5	5	1	1	0	0
I	10	10	5	5	1	1
Lanthanides	5000	5000	5000	5000	500	500
Ni	100	100	100	100	10	10
Nb	1000	1000	1000	1000	100	100
Np	2000	5000	2000	5000	200	500
Pu	5000	5000	5000	5000	500	500
Ra	100	100	100	100	100	100
Sr	1	1	3	3	3	5
Tc	0	1000	0	1000	0	100
Th	5000	5000	5000	5000	500	500
U	1000	1000	1000	1000	100	100

The above table does not include Cs or Eu, two nuclides of potential concern at Zion. Cs is known to have low sorption on cements. This is due in part to competition for sorption sites with other ions (Na and K) that are released by the leaching from the concrete. Bradbury and Sarott (Bradbury 1995) provided K_d estimates for Cs as 2 to 20 ml/g with the low value in Environment I. This is lower than the site-specific value for Cs at Zion. They also provided estimates for Eu (5000 to 1000 ml/g) with Environment III with the lowest K_d and Cm (5000 to 1000 ml/g) with Environment III providing the least sorption (Bradbury, 1995). A recent study (Felipe-Sotello, 2012) measured Kd values for Eu at 66000 ml/g. Other values for distribution coefficients in cementitious materials are provided in (Kaplan, 2008).

Discussion

Site-specific values are the most representative of the conditions that will occur at Zion after decommissioning and they will be recommended for use in groundwater dose assessment.

Although a final determination of the backfill material has not been made, it is likely that the backfill will contain a substantial amount of cementitious material. Examining the representative K_d values for soils (Table 3) and cementitious systems (Table 4) it is clear that with the exception of Cs the cement K_d values are greater than for soil systems. The K_d value selected is meant to provide a conservative assessment of dose to the groundwater pathway. For this reason, with the exception of H and Tc literature soil K_d values will be recommended for the assessment when site-specific values are not available. To increase the degree of confidence that a conservative value has been selected the 25th percentile K_d from either the NRC or Sheppard reports will be used. For Tc the sand K_d in Table 3 is less than 0.1. The cementitious oxidizing conditions K_d is zero in Table 4. The soil K_d is rounded to zero to ensure conservatism. The same will be done for the Table 3 H K_d as a conservative assumption.

For one nuclide, Sb-125, the IAEA median value was lower than the 25th percentile value on the NRC distribution. No standard deviation was reported in the Sheppard data. For this reason, the IAEA value is recommended as the appropriate value for screening calculations for Sb-125.

The recommended values for the basement fill model are either site-specific or values measured in soil. The K_d values in a cement environment for elements other tan Cs, Tc and H are expected to be higher based on existing data. Thus, they should be appropriate for outside of the buildings in the surrounding soil with the exception of H, Tc and Cs. Depending on the buffering capacity of the soil, time, and distance from the building, the chemical environment of the groundwater exiting the building may control the sorption of Cs. For this reason, the site-specific Kd for Cs in the cement environment should be used in the surrounding soils to provide a conservative estimate of groundwater concentration for dose assessment.

Recommended Values

The values in Table 5 are the minimum values found in any test for the site-specific case and the minimum values found from the reports cited in Table 3. These values are appropriate for maximizing the groundwater concentration and thereby predicted dose. For intruder scenarios or scenarios where the backfill is used as gardening soils, a higher value of K_d would be recommended for maximizing the predicted dose in those cases.

Table 5 Recommended K_d values to be used in the basement fill model.

Radionuclide	Half Life (years)	Recommended Basement Fill K_d ml/g	Reference[1]
H-3	1.24E+01	0	[2]
C-14	5.73E+03	1.2	NRC, 2000
Fe-55	2.70E+00	2857	Site-Specific
Ni-59	7.50E+04	62	Site Specific
Co-60	5.27E+00	223	Site Specific
Ni-63	9.60E+01	62	Site Specific
Sr-90	2.91E+01	2.3	Site Specific
Nb-94	2.03E+04	45	NRC, 2000
Tc-99	2.13E+05	0	[2]
Ag-108m	1.27E+02	27	Sheppard, 1990
Sb-125	2.77E+00	17	IAEA, 2010
Cs-134	2.06E+00	45	Site Specific
Cs-137	3.00E+01	45	Site Specific
Pm-147	2.62E+00	95	NRC, 2000
Eu-152	1.33E+01	96	NRC, 2000
Eu-154	8.80E+00	95	NRC, 2000
Eu-155	4.96E+00	95	NRC, 2000
Np-237	2.14E+06	1	Sheppard, 1990
Pu-238	8.77E+01	174	Sheppard, 1990
Pu-239/240	2.41E+04	174	Sheppard, 1990
Pu-241	1.44E+01	174	Sheppard, 1990
Am-241	4.32E+02	177	NRC, 2000
Am-243	7.38E+03	177	NRC, 2000
Cm-243/244	2.85E+01	891	Sheppard, 1990

[1] Values from NRC, 2000 or Sheppard, 1990 are the 25th percentile values on the cumulative distribution function.
[2] 25th percentile value was less than 0.1 and was rounded down to 0.

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